JOURNAL OF CATALYSIS 77, 554–557 (1982)

Vapor-Phase Direct Hydration of Ethylene over Zirconium Tungstate Catalyst

II. Catalytic Behavior at High Pressures

We recently reported that zirconium tungstate (ZrW) having a molar composition of W/Zr = 2.0 efficiently catalyzed the vapor-phase direct hydration of ethylene at atmospheric pressure, and discussed the catalytic behavior of ZrW in connection with kinetic consideration (*1*). Commercial ethylene hydration processes are usually operated at 60–80 kg/cm^2. In order to examine practical applicability of the ZrW catalyst, this paper describes the catalytic features of ZrW in the ethylene hydration reaction under elevated pressures; the effects of the reaction variables (pressure, H_2O/C_2H_4 mole ratio, space velocity) on the yields of ethanol and by-products (acetaldehyde, diethyl ether, butenes) are discussed.

The ZrW (W/Zr = 2.0) was prepared according to the previous method (*1*). The reaction was carried out in a flow system (Fig. 1). The catalyst (15–50 ml, 16–42 mesh) was placed in the middle part of the reactor (H) (stainless steel, 28ϕ × 600 mm). Both the remainder of the reactor and the preheater (G) (stainless steel, 28ϕ × 340 mm) were packed with pieces of stainless-steel helix. The temperatures were controlled and measured by use of Chromel–Alumel thermocouples. The reactor and the preheater were heated by means of electric furnaces under nitrogen atmosphere. When each temperature attained a prescribed level, nitrogen was pressurized up to the reaction pressure and flowed at a rate between 40 and 60 nl/h. At the same time water was added to the reactor by a plunger pump (E). Then the nitrogen stream was switched to the pressurized ethylene stream which passed through a rotameter (D). A gaseous mixture of the products from the reactor was air-cooled. Most of the mixture was collected in a separator (J) maintained at a constant temperature (e.g., 20°C at 70 kg/cm^2) and the rest was discharged together with the unreacted ethylene. The liquid products in the separator and the off-gas were analyzed at every 1-h interval by GLC using columns of PEG-1000 on Flusin T (1.5 m) and Porapak-Q (2 m). The steady formation of ethanol was usually observed after 2–3 h of reaction.

FORMATION OF ETHANOL

(*a*) *Effect of Reaction Pressure*

At each pressure, the yield of ethanol (moles of C_2H_5OH formed per mole of C_2H_4 fed, in percent) increased with temperature, passed through a maximum, and then decreased owing to equilibrium limitation (Fig. 2). The maximum yield increased with pressure shifting toward higher temperature. The discrepancy between the observed yield under the equilibrium limitation and the theoretical yield that was calculated according to Ewell's method (*2*) became greater at higher pressures. This is ascribed partly to the by-products. However, the amount of the by-products was not so great as to correspond to the discrepancy. The ZrW was found to have the maximum pore-size distribution at around 13 Å radius from the measurement according to the methanol adsorption method (*3*). Under the present reaction conditions, this pore size appears to be small enough to cause

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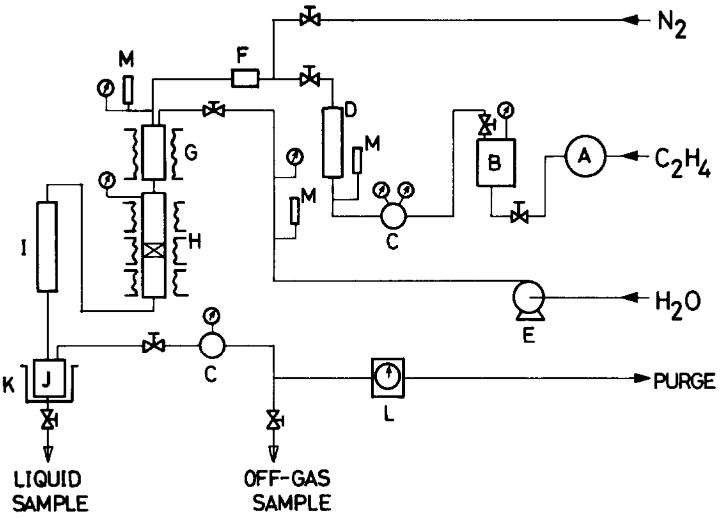

FIG. 1. Diagram of the reaction system. A: Compressor; B: reservoir; C: pressure regulator; D: rotameter; E: plunger pump; F: flow control valve; G: preheater; H: reactor; I: cooler; J: separator; K: water jacket; L: wet test meter; M: safety valve.

capillary condensation of water vapor on the catalyst surface. Thus it is probable that at a space velocity of 2300 h^{-1} the reaction is still also kinetically controlled even at higher temperatures and retarded by the increasing condensation of water at higher pressures. The reverse effect of pressure observed below ca. 250°C (kinetic control region) may be elucidated also in terms of the increasing condensation of water vapor with the increase in pressure.

(*b*) *Effect of Water-to-Ethylene Mole Ratio*

The effect of H_2O/C_2H_4 ratio on the yield of ethanol at 280°C and 70 kg/cm^2 is shown in Fig. 3. At any space velocity (SV), the yield of ethanol increased and the corresponding space–time yield (STY) decreased with the H_2O/C_2H_4 ratio. There

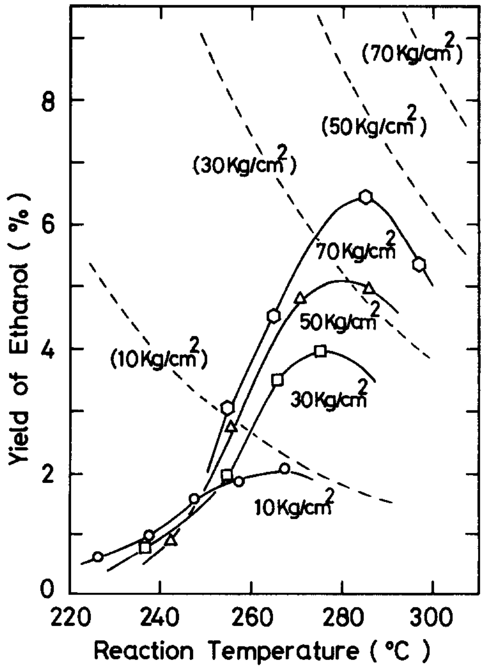

FIG. 2. Effects of reaction temperature and pressure on the yield of ethanol. H_2O/C_2H_4 mole ratio: 1.0; SV: 2300 h^{-1}.

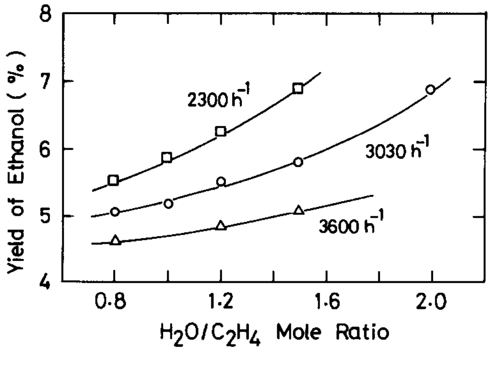

FIG. 3. Effect of H_2O/C_2H_4 mole ratio on the yield of ethanol. Temperature: 280°C; pressure: 70 kg/cm^2.

should be an optimum H_2O/C_2H_4 ratio since both the yield and the STY are important factors in process design.

(*c*) *Effect of Space Velocity*

The yield of ethanol at each temperature decreased with SV (Fig. 4). It is noted that the yield at a temperature below 270°C decreased rapidly at higher SVs. This is possibly due to the poisonous adsorption of water at lower temperatures as discussed above.

FORMATION OF BY-PRODUCTS

In almost all runs, by-products included acetaldehyde (AcH), diethyl ether (Et_2O), and butenes. Oily substances such as ethylene oligomers were not detected.

(*a*) *Acetaldehyde*

The formation of acetaldehyde is illustrated in Fig. 5. At each pressure acetaldehyde increased significantly above the temperature where the yield of ethanol became maximum (vide supra). This fact suggests that acetaldehyde is formed by the dehydrogenation of ethanol over the ZrW catalyst which may be expected to reveal dehydrogenation activity like that of tungsten oxide catalysts. Also the fact that the acetaldehyde formation was suppressed with increasing pressure supports the dehydrogenation mechanism. However, the amount of hydrogen in the off-gas stream was too small to be detected.

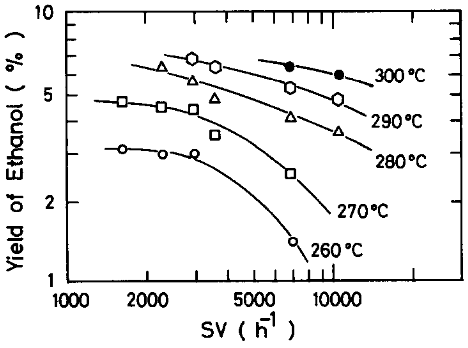

FIG. 4. Effect of space velocity on the yield of ethanol. H_2O/C_2H_4 mole ratio: 1.2; pressure: 70 kg/cm^2.

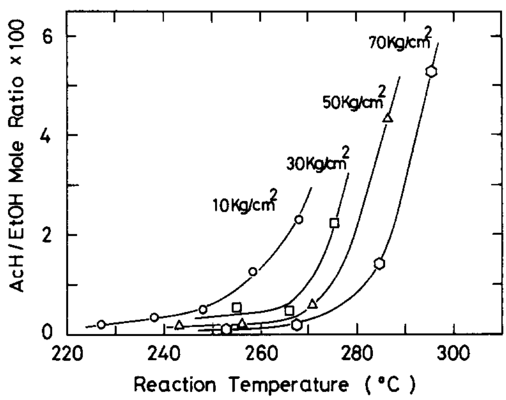

FIG. 5. Effects of reaction temperature and pressure on the ratio of acetaldehyde to ethanol. H_2O/C_2H_4 mole ratio: 1.0; SV: 2300 h^{-1}.

Another experiment indicated that the ZrW underwent reduction with ethanol to a certain degree. The present reaction, therefore, involves the stoichiometric oxidation of ethanol to acetaldehyde with the ZrW catalyst. In fact a significant amount of acetaldehyde was detected just after the start of the reaction. However, its steady formation was attained within several hours on-stream, which means the occurrence of the catalytic dehydrogenation of the product ethanol during the reaction.

(*b*) *Diethyl Ether*

In every run the equilibrated amount of diethyl ether was formed. The equilibration of the dehydration of ethanol into the ether was ascertained by the facts that the equilibrium constant calculated from the product compositions depended only on the reaction temperature and the constant did not change with the prior addition of the ether to the feeds. The equilibrium constant of the dehydration was 2.6 at 280°C.

(*c*) *Butenes*

Butenes, which were formed by ethylene dimerization, consisted of *trans*-2-butene as a major component and *cis*-2-butene and 1-butene as minor components. The total yield of butenes increased noticeably with temperature (0.1–0.4 mole% of C_2H_4 fed). At a constant temperature, higher H_2O/C_2H_4 ratio reduced the dimerization reaction.

SELECTIVITY

Among the many kinds of by-products in ethylene hydration, both acetaldehyde and diethyl ether would cause no serious loss of ethylene in practical operation, because acetaldehyde can be converted to ethanol by a subsequent hydrogenation process (*4*) and diethyl ether can be recycled to the hydration reactor at an equilibrium composition (*5*). The by-products leading to the loss of ethylene, therefore, are represented by ethylene oligomers which include butenes and by their related compounds such as higher alcohols and aldehydes. In our experiments, however, such by-products, except butenes, were not detectable. Thus the selectivity of ethylene to ethanol should be defined as follows:

Selectivity (mole%) = [moles of C_2H_4 converted to $(C_2H_5OH + CH_3CHO)] \times 100/$ [moles of C_2H_4 converted to $(C_2H_5OH + CH_3CHO + C_4H_8)]$.

The ZrW catalyst gave a quite high selectivity (94–99 mole%) at high H_2O/C_2H_4 ratios (1.2–1.8) and high SVs (2300–10,600 h^{-1}).

In conclusion, the ZrW catalyst was found to perform excellently in the vapor-phase direct hydration of ethylene under practical operating conditions.

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HIROO MOMOSE
KOSHI KUSUMOTO
YUSUKE IZUMI[1]
YUKIO MIZUTANI

Fujisawa Research Laboratory
Tokuyama Soda Company, Ltd.
2051 Endo, Fujisawa City
Kanagawa 252, Japan

Received July 13, 1981; revised April 18, 1982

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[1] Present address: *Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan.*